Oxygen grain-boundary transport in polycrystalline alumina using wedge-geometry bilayer samples: Effect of Y-doping

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Abstract

Novel wedge-geometry, dual-layer alumina samples, both undoped and 500 ppm Y³+-doped, were studied in the temperature regime 1250–1400 °C to determine the effect of Y³+ on oxygen grain-boundary transport in alumina. The samples consisted of a wedge-shaped, single-phase alumina top layer, diffusion bonded to an alumina/Ni substrate containing a fine, uniform dispersion of Ni marker particles (0.5 vol.%). The extent of the alumina spinel oxidation layer was measured as a function of the wedge thickness for a series of heat-treatment conditions. Models of the transport behavior were used to derive values for the rate constants (k) in both the alumina top layer and the alumina/Ni substrate. It was found that the presence of yttrium slows oxygen grain-boundary diffusion in alumina by a factor of \( \frac{1}{24} \) (at 1300 °C), and increases the corresponding activation enthalpy for oxidation from \( 407 \pm 20 \) to \( 486 \pm 34 \) kJ mol⁻¹. Microstructural observations suggested that yttrium also slows Ni outward diffusion. A comparison of the different k values revealed that, at 1300 °C, the presence of Ni alone enhances transport by a factor of \( \frac{1}{24} \) relative to undoped alumina.

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1. Introduction

The addition of reactive elements (RE) to polycrystalline alumina results in enhancement of creep resistance [1–3], suppression of sintering and densification processes [4–6], retardation of the grain growth rate [5] and improvement in the adhesion of alumina scales [7–9]. From a technological perspective, materials with RE additions for thermal barrier coatings that are used in turbine engines are of considerable interest because slow-growing alumina scales formed on alloy surfaces can protect the underlying substrate from further oxidation, thereby improving engine lifetime. It is believed that the formation of alumina scales is controlled by oxygen inward diffusion and/or aluminum outward diffusion along the grain boundaries. The addition of RE, such as yttrium [10,11], is thought to modify the relative importance of diffusion paths and the relative diffusion rates of aluminum and oxygen by “blocking” nominal fast paths [12,13] and/or by locally changing the bond strength in the vicinity of the dopant ions [14–16]. The extent to which RE additions affect anion and cation diffusion, respectively, remains unclear, however. Some workers [17–27] have suggested that RE doping blocks the outward transport of aluminum ions and reduces cation transport through the scales, resulting in growth primarily by inward oxygen diffusion, while others [28,29] have proposed that doping primarily retards oxygen diffusion. Thus, careful
A conventional method for studying oxygen grain-boundary diffusion in alumina is via the combination of a two-stage oxidation method and the secondary ion mass spectrometry (SIMS) technique [30–34]. In particular, alloys are first oxidized in an $^{16}\text{O}$ atmosphere until an alumina layer of a prescribed thickness is formed on the surface. Subsequently, the whole specimen is annealed in an $^{18}\text{O}$-enriched gas, and the $^{18}\text{O}$ concentration profile is obtained using SIMS. The oxygen grain-boundary diffusion coefficient is then calculated according to the classic Whipple–Le Claire equation [35].

Despite its widespread use, the results obtained by different groups employing this method have been inconsistent. For example, Pint [36] studied the oxidation behavior of an oxide-dispersion-strengthened (ODS) FeCrAl alloy at 1200 °C by thermogravimetry. The results indicated that the rate constant of ODS-FeCrAl alloy was reduced by a factor of 2–3 relative to that of undoped FeCrAl alloy. In earlier work, Balmain et al. [30] investigated the transport properties of alumina scales formed on undoped and Y-doped $\beta$-NiAl at 1100 °C by both the thermogravimetry method and the SIMS technique. The latter analysis showed that the oxygen grain-boundary diffusivity was lowered by a factor of three with the presence of yttrium, while the former analysis showed that the rate constant for the oxidation of Y-doped $\beta$-NiAl was lowered by a factor of five relative to the undoped case. Hou [37] summarized the results of experimental studies of alloy oxidation rates and showed that RE additions in Ni- and Fe-based alloys typically reduce the oxidation rate by a factor of $\approx 2$ to 4, but it remains unclear which type of RE is most effective in suppressing oxidation.

These findings can be contrasted with those of two other studies. In particular, Prot et al. [38] found a two orders of magnitude decrease in the oxygen grain-boundary diffusivity with yttrium doping in their transport study of undoped and Y$^{3+}$-doped alumina polycrystals in the temperature range 1460–1720 °C. In addition, an investigation of the oxidation behavior of Ni$_3$Al alloy (with and without yttrium) showed that yttrium had little to no effect on the growth rate of the scale in the temperature range 900–1200 °C [39]. In short, differences in alloy composition, type and concentration of RE, and heat-treatment conditions complicate the comparison of oxidation rates among different groups. Indeed, Heuer [40] recently concluded that, based on a critical survey of the literature, understanding of grain-boundary diffusion in alumina is woefully incomplete.

Thus, this work systematically examined oxygen grain-boundary transport in both undoped and Y$^{3+}$-doped alumina using a novel experimental method, namely a wedge-shaped bilayer geometry which permits the analysis and correlation of effectively independent diffusion profiles. Alumina samples were made from ultra-high-purity starting powders to mitigate unwanted impurity effects. This fabrication method not only circumvents the scale spallation and growth stress of alumina scale which attend the oxidation of alloys, but averages grain-boundary diffusivities for many sampled grains, by contrast with SIMS (<1000 grains within 100 nm depth [38]).

This study is an extension of previous investigations [41] in which the oxidation of undoped and 500 ppm Y$^{3+}$-doped alumina (with 0.5 vol.% Ni dispersion) in a monolithic test geometry was studied. The results showed that the presence of yttrium reduced the rate constants by a factor of six at 1300 °C. Meanwhile, preliminary analytical electron microscopy (AEM) analysis in those samples showed the segregation of Ni along the grain boundaries. Motivated by these results, a sample with a wedge-shaped alumina top layer on an alumina/Ni substrate was designed to isolate the effect of Ni markers on the diffusive process. Following heat treatment in an oxidizing atmosphere, inward diffusion of oxygen results in the oxidation of the Ni particles to form nickel aluminate spinel (NiAl$_2$O$_4$). By modeling the relationship between the diffusion length in the alumina layer and that in the alumina/Ni substrate, it was possible to derive transport rate constants for the different layers in both undoped and Y-doped specimens. Furthermore, assuming that diffusion in this system is essentially one-dimensional, the wedge-geometry permits, in effect, a multitude of parallel diffusion experiments with a range of layer thicknesses. A self-consistent comparison of the resulting diffusion profiles then leads to robust estimates of the kinetic parameters.

2. Experimental procedure

2.1. Materials and sample geometry

A novel wedge-shaped, bilayer specimen was used to study oxygen grain-boundary transport in alumina. As shown in Fig. 1, the sample consisted of a wedge-shaped layer of polycrystalline, single-phase alumina, diffusion bonded to a polycrystalline alumina substrate containing a uniform fine dispersion of Ni marker particles (with $V_i \approx 0.5$ vol.%). Bilayer samples were studied in which
both the wedge and substrate layers were either (i) doped with 500 ppm Y or (ii) undoped.

2.2. Sample preparation

High-purity alumina powder with a quoted mean particle size of 0.2 μm (Sumitomo Chemical Co. Ltd, Japan, >99.99%) was hot-pressed at 1250 °C for 10 h at 45 MPa at an atmospheric pressure of <60 mtorr. The as-hot-pressed sample was cut into ~3 mm thick slices. One side of a slice was polished down to 1 μm, and the other side was ground until both sides were parallel. The as-hot-pressed alumina/Ni composite was made following the procedure described in an earlier paper [41]. After hot-pressing, it was also cut into ~3 mm thick slices, polished and ground as outlined above. In order to mark the original position of the bilayer interface, several narrow strips of a thin Ir coating (width ~0.5 mm, thickness ~50 nm) were sputtered onto the polished surface of the alumina/Ni composite prior to joining (EMS 575 Turbo Sputter Coater, EMS, Hatfield, PA). The alumina and alumina/Ni samples were then assembled with the polished sides facing each other, and subsequently hot-pressed at 1250 °C for 12 h at 45 MPa at an atmospheric pressure <60 mtorr. The as-hot-pressed bilayer sample was then cut into small rectangular pieces (~8 x 3 x 3 mm³). Each piece was glued (alumina layer facing outwards) onto a 3° inclined surface of a stub (Fig. 2a). First, the alumina layer was ground using a 10 μm fixed diamond disk until a small area of the alumina layer on one side was removed; the surface was then polished to a 1 μm finish (Fig. 2b). This procedure was adopted to ensure that the depth of the alumina layer started from zero and increased gradually. It also minimized the possible influence of oxygen diffusion from the side of the sample.

To fabricate doped specimens, 500 ppm Y³⁺-doped alumina powder was hot-pressed at 1300 °C for 12 h at 45 MPa at an atmospheric pressure of <60 mtorr. These conditions were chosen to obtain doped specimens with an average grain size close to that of the as-hot-pressed alumina specimen. Note that, although the hot-pressing temperature was 50 °C higher for the Y³⁺-doped samples, it is assumed that re-equilibration of the segregant ions takes place at the temperature of annealing. A 500 ppm Y³⁺-doped alumina/Ni composite was also fabricated as described previously [41]. Joining of the layers was achieved by hot-pressing at 1300 °C for 15 h at 45 MPa, at an atmospheric pressure of <60 mtorr. All other procedures and processing conditions were the same as those described previously for the undoped samples. The maximum residual porosity of the as-hot-pressed specimens, both undoped and Y³⁺-doped, was <3%.

2.3. Oxidation of samples and determination of diffusion depth

The top alumina layers of the wedge samples were polished down to a 1 μm diamond finish using an automated polishing machine. The samples were cleaned in an ultrasonic bath using first acetone, then ethyl alcohol followed by deionized water, for 30 min each. After cleaning, a wedge specimen was placed in an alumina crucible (99.8%, Vesuvius McDanel, Beaver Falls, PA) with high-purity alumina powder around it. Oxidation of the samples was carried out in an oxygen-flow tube furnace in the temperature range 1250–1400 °C for a specified period of time. Finally, the samples were sectioned and polished again down to 1 μm. Fig. 3 shows an optical micrograph of the cross section of the Y³⁺-doped wedge sample oxidized at 1300 °C for 190 h (Nikon Instruments, Inc., Melville, NY). The region where the Ni particles were oxidized appeared greenish, and the depth of the alumina/spinel layer decreased with increasing depth of the top alumina layer, as expected.

Preliminary experiments revealed that SEM images recorded using backscattered electrons (BSEs) yielded the greatest contrast between oxidized (alumina–spinel) and non-oxidized (alumina–Ni) regions. Fig. 4 shows a cross section of an undoped wedge sample that was oxidized for 20 h at 1350 °C and examined under SEM using BSE contrast. The thickness of the alumina wedge layer x and
that of the corresponding alumina/spinel layer \( y \), as shown in the figure, were determined as follows: A line of length \( x \) was drawn perpendicular to the interface to a point \( A \); the position of \( A \) was determined such that, for a material slice of thickness \( D \) extending from \( x - \Delta x \) to \( x \), the number density of spinel particles in the area \([ l \times \Delta x] \) was essentially zero, while for that of thickness \( D \) extending from \( x \) to \( x + \Delta x \), spinel was uniformly distributed, where \( l \) (\( \sim 10 \) \( \mu \)m) is a horizontal distance centered on \( A \). The value of \( \Delta x \) was set (somewhat arbitrarily) as \( \sim 5 \) \( \mu \)m, a distance which corresponds approximately to two alumina grain diameters (before incorporating a stereological factor of 1.5 [42]). Having determined \( x \), a second line was drawn from \( A \) with length \( y \), such that, by moving a distance \( \Delta y \) away from the surface, the ratio of the number of Ni particles to that of spinel in the area \([ l \times \Delta y] \) was \( > 50 \% \). Similarly, by moving \( \Delta y \) toward the surface, the corresponding ratio was \( < 50 \% \). Again, the value of \( \Delta y \) was set as \( \sim 5 \) \( \mu \)m.

3. Results

3.1. Microstructure

As described earlier, the bilayer sample geometry consisted of an upper wedge layer of single-phase alumina bonded to an alumina substrate containing a dispersion of Ni particles. Two sets of samples were studied: in one case, both layers were doped with 500 ppm Y\(^{3+}\) and, in the other case, both layers were undoped. In Fig. 4, the original position of the interface between the two layers is delineated by a thin layer of iridium. A reaction layer consisting of alumina and spinel second phase can be seen between the upper alumina layer and the alumina/Ni substrate. Note that the BSE intensity scales with the mean atomic number; hence, the bright contrast of the Ni particles.

The average grain sizes of the undoped and Y\(^{3+}\)-doped wedge samples, both in the as-hot-pressed condition and after the heat treatment, were determined using the linear intercept method, incorporating a stereological factor of 1.5. The values are listed in Table 1 for both the wedge layer and the alumina/Ni substrates. In order to evaluate the maximum extent of grain growth during the oxidation anneal, grain sizes were determined for the longest heat-treatment time at each temperature. It can be seen that, for the Y\(^{3+}\)-doped sample, the size of the alumina grains in both layers was within experimental scatter. This was the case in the as-hot-pressed condition, and for all the heat-treatment temperatures studied. As expected, the greatest extent of grain growth was for the highest heat-treatment temperature (1400 \(^{\circ}\)C). Specifically, after 80 h at 1400 \(^{\circ}\)C, the increases in size for the grains in the wedge layer and the alumina/Ni substrate were \( \sim 21 \% \) and 15\%, respectively. For the undoped sample, the size of the alumina grains in the top layers was larger than that in the alumina/Ni substrate by a factor of \( \sim 1.4 \).

3.2. Simplified transport models

Before performing a more detailed analysis of the transport kinetics in this system, it is useful first to assess the validity of a quasi-steady-state model of diffusion. As will be seen below, this simplified description, as well as its limitations, yields important information regarding the relative diffusion coefficients in the wedge and the underlying substrate. For a given temperature, the quasi-steady-state assumption is valid when the maximum depth of the alu-

![Fig. 4. Scanning electron micrograph showing the cross section of the undoped wedge sample after oxidation at 1350 \(^{\circ}\)C for 20 h (backscattered electron contrast).](image-url)
minas layer is smaller than a characteristic oxygen diffusion length $x_c$, which is a function of the grain-boundary diffusivity $D_{gb}$, such that $x_c \sim \sqrt{2D_{gb}t_c}$, where $t_c$ is the characteristic time.

Consider the schematic of the bilayer system shown in Fig. 5. It is assumed that diffusion through the alumina layer at each location is essentially one-dimensional ($z$), and that an interface at a fixed position $x$ separates the $\text{Al}_2\text{O}_3$ and underlying layers. For the pseudo-steady-state model ($C(z = x + y) = 0$), given the diffusivities $D_1$ and $D_2$ in these layers, respectively, and the oxygen concentration $C(z)$ at the surface, $C(z = 0) = C_s$, and at the layer interface, $C(z = x) = C_1$, respectively, the continuity of flux requires that

$$-D_1 \left( \frac{C_1 - C_s}{x} \right) = -D_2 \left( \frac{0 - C_1}{y} \right) = C_{\text{Ni}}^0 \left( \frac{dy}{dt} \right)$$

where $y$ is the depth of the oxidized (i.e. $\text{Al}_2\text{O}_3$/spinel) layer and $C_{\text{Ni}}^0$ is the initial Ni concentration. Upon eliminating $C_1$ and then integrating, one obtains

$$\frac{y^2}{t} = k_2 - 2 \left( \frac{k_2}{k_1} \right) \frac{xy}{t}$$

where the rate constants $k_1 = (2C_s/C_{\text{Ni}}^0)D_1$ and $k_2 = (2C_s/C_{\text{Ni}}^0)D_2$.

To determine the range of validity of this analysis, it is useful to examine Fig. 6, in which $y^2$ is plotted vs. $xy$ for a wedge sample oxidized at 1350 °C for 60 h. From Eq. (2), the plot is expected to be linear in the steady state. It is noted that the resulting curve has a linear regime for only a limited range of $x$ (and therefore a limited range of $y$). A linear regression for this portion of the curve yields the fitting line (and hence $D_2/D_1$) shown in the figure. For smaller values of $y$, there is clearly a substantial deviation from linearity. These results can be understood as follows. For relatively small values of the wedge thickness ($x$), the steady-state approximation is acceptable since, for the given time and temperature, the characteristic oxygen diffusion length exceeds $x$. For $x > x'$, where $x'$ locates the nose of the curve, the pseudo-steady state has not been reached, and transient behavior is observed. In reality, of course, there is a narrow range of $x$ values over which this transition occurs but, for simplicity, one critical value is identified, namely $x'$, where $x' \approx x_c$.

The diffusive behavior of the wedge system in the transient regime can be modeled simply by assuming that $C_t$ is essentially zero for cases in which $x > x'$. Thus, in this limit, one has that

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial z^2}$$

with the boundary conditions $C(z = 0, t) = C_s$, $C_1 = 0$, and the initial condition $C(z \neq 0, t = 0) = 0$. From the solution to this diffusion equation, one can calculate the total amount of oxygen per unit area that has crossed the top alumina layer at $z = x$, $j_o$, as [43]

$$j_o = C_{\text{Ni}}^0 x = C_s \left[ \frac{D_1 t}{x} + \frac{2x}{\pi^2} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n^2} \left( 1 - e^{-\frac{x^2}{4D_1 t}} \right) \right]$$

In the late-stage transient regime, where $t > x'^2/6D_1$, one obtains the approximate relation

$$\frac{\partial C}{\partial t} \approx \frac{C_s D_1}{x} \frac{1}{6C_{\text{Ni}}^0} \frac{x}{t}$$

The best fit for data points for which $x > x'$, based on Eq. (5), is also displayed in Fig. 6. Note that the value of $x'$ was estimated from the location of the nose of the curve and that the fitting parameters were relatively insensitive to the value of $x'$ chosen. It can be seen that, taken together, the two curve fits describe the data over a wide range of layer thicknesses. A more detailed analysis of diffusion kinetics in which the oxygen concentration profiles in the bilayer are obtained numerically is presented in the Appendix A.
3.3. Kinetic parameters

By applying the foregoing analysis to data sets acquired for oxidation heat-treatments at temperatures of 1250, 1300, 1350 and 1400 °C, values of $k_1$, $k_2$, $D_1$ and $C_{1}/C_{Ni}$ were obtained as functions of temperature. (In this notation, the subscript 1 denotes the outer wedge layer, and the subscript 2 denotes the alumina/Ni substrate.) These findings are summarized in Table 2 for both the undoped and Y$^{3+}$-doped samples over the range of temperatures studied. The stated uncertainties in the values of $k$ represent the spread in the $k$ values obtained at the same temperature, but for different heat-treatment times.

For the purposes of comparison, Fig. 7 presents plots of $y^2/t$ vs. $xy/t$ of the undoped wedge samples for a series of heat-treatments at different temperatures. It is evident that, as predicted by the model (see Eq. (2)), when the data are normalized with respect to time, the graphs form a series of inverse ‘C’-shaped curves which roughly superpose for the separate annealing temperatures 1250, 1300 and 1350 °C. For heat-treatment at 1400 °C, however, this scaling breaks down, and it is possible that grain growth and/or the increased mobility of Ni (1400 °C is $\approx$0.97 $T_m$, where $T_m$ is the melting point of pure Ni) are additional factors that complicate the description of transport at higher temperatures.

To analyze the oxidation kinetics, the logarithm of the rate constants was plotted vs. the reciprocal of the absolute temperature in Fig. 8, and the expected Arrhenius behavior was obtained. The activation enthalpy for oxidation, $E$, were determined from a least-squares fit to these plots, and the values corresponding to the different material layers are tabulated in Table 3. In the case of the undoped and 500 ppm Y$^{3+}$-doped alumina outer wedge layers, the activation enthalpies were found to be $E_1(u) = 407 \pm 20$ kJ mol$^{-1}$ and $E_1(Y) = 486 \pm 34$ kJ mol$^{-1}$, respectively. For the undoped and 500 ppm Y$^{3+}$-doped alumina/Ni substrate layers, the corresponding values were determined as $E_2(u) = 381 \pm 30$ kJ mol$^{-1}$ and $E_2(Y) = 489 \pm 37$ kJ mol$^{-1}$, respectively. (The errors in the activation enthalpies represent confidence intervals of 95% [44].) It can be seen that the values for the undoped layers ($E_1(u)$, $E_2(u)$) agree within experimental scatter, and similarly for the Y-doped layers ($E_1(Y)$, $E_2(Y)$). This agreement implies, in turn, that the presence of Ni does not significantly influence the activation enthalpies.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>1250</th>
<th>1300</th>
<th>1350</th>
<th>1400</th>
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<tbody>
<tr>
<td>Undoped</td>
<td></td>
<td></td>
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<tr>
<td>$C_{1}/C_{Ni}$</td>
<td>0.49 ± 0.03</td>
<td>0.40 ± 0.12</td>
<td>0.41 ± 0.16</td>
<td>0.19 ± 0.01</td>
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<tr>
<td>$D_1$ (m$^2$ s$^{-1}$)</td>
<td>(8.46 ± 0.53) × 10$^{-15}$</td>
<td>(3.41 ± 1.39) × 10$^{-14}$</td>
<td>(8.31 ± 2.34) × 10$^{-14}$</td>
<td>(2.77 ± 0.73) × 10$^{-13}$</td>
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<tr>
<td>Ratio</td>
<td></td>
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<tr>
<td>$k_1/k_1$ (Y)</td>
<td>3.03 ± 0.55</td>
<td>2.21 ± 0.66</td>
<td>1.46 ± 0.69</td>
<td>1.46 ± 0.69</td>
</tr>
<tr>
<td>$k_2(Y)/k_1(Y)$</td>
<td>0.94 ± 0.26</td>
<td>1.06 ± 0.37</td>
<td>0.99 ± 0.21</td>
<td>0.99 ± 0.21</td>
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<tr>
<td>$k_2/k_1$</td>
<td>2.37 ± 0.45</td>
<td>2.91 ± 0.53</td>
<td>2.83 ± 0.64</td>
<td>2.05 ± 1.55</td>
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<tr>
<td>Y-doped</td>
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<tr>
<td>$k_2(Y)$ (m$^2$ s$^{-1}$)</td>
<td>(9.35 ± 1.24) × 10$^{-15}$</td>
<td>(3.52 ± 0.43) × 10$^{-14}$</td>
<td>(9.02 ± 0.82) × 10$^{-14}$</td>
<td>(9.14 ± 0.94) × 10$^{-14}$</td>
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<tr>
<td>$k_1(Y)$ (m$^2$ s$^{-1}$)</td>
<td>(9.91 ± 1.06) × 10$^{-15}$</td>
<td>(3.32 ± 0.55) × 10$^{-14}$</td>
<td>(9.14 ± 0.94) × 10$^{-14}$</td>
<td>(9.14 ± 0.94) × 10$^{-14}$</td>
</tr>
<tr>
<td>Undoped</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$ (m$^2$ s$^{-1}$)</td>
<td>(2.39 ± 0.29) × 10$^{-14}$</td>
<td>(8.74 ± 0.99) × 10$^{-14}$</td>
<td>(2.08 ± 0.26) × 10$^{-13}$</td>
<td>(2.72 ± 0.52) × 10$^{-13}$</td>
</tr>
<tr>
<td>$k_1$ (m$^2$ s$^{-1}$)</td>
<td>(1.01 ± 0.06) × 10$^{-14}$</td>
<td>(3.00 ± 0.17) × 10$^{-14}$</td>
<td>(7.35 ± 0.61) × 10$^{-14}$</td>
<td>(1.33 ± 0.43) × 10$^{-13}$</td>
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Fig. 7. Graphs showing the relationship at different temperatures between the square of the oxidized layer thickness ($y^2$), and the product of $y$ with the depth of the alumina wedge layer ($x$); the quantities on both axes were normalized with respect to the annealing time ($t$).
a result that was confirmed at the 5% level of significance by applying a standard statistical test of the equality of means.

4. Discussion and conclusions

In this work, oxygen grain-boundary diffusion in a novel wedge-shaped, bilayer specimen, for both undoped and 500 ppm Y$^{3+}$-doped alumina, was investigated in the temperature range 1250–1400 °C. Two mathematical models were used to fit the experimental data and extract rate constants ($k$) in both the alumina top layers and the alumina/Ni substrates. As part of this analysis, values for both the oxygen solubility in alumina, $C_s$, and the apparent oxygen grain-boundary diffusivity, $D_1$, in the undoped alumina top layer, were obtained. For example, at 1300 °C, with 0.5 vol.% Ni and $C_s/C_{Ni} = 0.4$, $C_s$ was calculated as $3.04 \times 10^{-4} \text{ mol cm}^{-3}$. The apparent oxygen diffusivity in undoped alumina ($D_1$) was found to be $\sim 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at 1300 °C. Unfortunately, a direct comparison of this result with the values obtained by other groups is problematic, owing to differences in experimental procedures and material systems. For example, the measured diffusivity values for alumina polycrystals obtained using SIMS are significantly lower than those deduced from rate constants using Wagner’s theory, determined from oxidation experiments on alumina-forming alloys. Indeed, these differences can be as high as four orders of magnitude [32]. In comparing the results of different studies, therefore, the focus will be on the ratios of diffusivities or rate constants for doped and undoped alumina. As will be seen from the following, a comparison of the $k$ values for the different material layers yields valuable information on the influence of additive elements on oxygen transport in alumina.

Consider first the ratio of $k_1/k_1(Y)$, which reflects the influence of yttrium on oxygen transport in alumina in the absence of nickel particles. It can be seen that, over the range of temperatures studied, the rate constant is greater by up to a factor of three at 1300 °C in the undoped alumina layer. However, the average grain size $d$ in the undoped alumina layer was consistently larger than that of the Y$^{3+}$-doped layer (i.e. $d_1/d_1(Y) \approx 1.6$, where $d$ is the grain size). Assuming grain-boundary transport is dominant, the apparent diffusivity will scale with the inverse of the grain size and, if a grain-size correction is applied, it can be seen that the existence of yttrium reduces oxygen grain-boundary diffusion in alumina by up to a factor of 5 (that is, $3 \times 1.6$) at 1300 °C. Smaller decreases in the diffusivity due to doping occur at higher heat-treatment temperatures. The results in this work are more consistent with those obtained from oxidation of alloys, where a reduction

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Table 3

<table>
<thead>
<tr>
<th>Activation enthalpies for oxidation in alumina.</th>
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<td></td>
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<tr>
<td>$E$ (kJ mol$^{-1}$)</td>
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<td>430 ± 40</td>
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Fig. 8. Arrhenius plots of the rate constants for (a) the alumina layer and (b) the alumina/Ni substrate of wedge samples, both undoped and 500 ppm Y$^{3+}$-doped. (The solid lines are least-squares fits to the data.)
of a factor of 2–9 in the rate constant is observed for alumina scales [7,27,30,36,45,46]. In this regard, the results of SIMS studies of oxygen grain-boundary diffusion in alumina, which indicate that the diffusivity is reduced by two orders of magnitude upon doping with yttrium [38], are outliers.

Consider next the influence of nickel on oxygen transport. From Table 2 it can be seen that at 1300 °C, \( k_2/k_1 \) is \( \sim 3 \). However, the grain size in the alumina wedge layer was larger than that of the substrate (\( d_1/d_2 \approx 1.4 \)). If the ratio \( k_2/k_1 \) is corrected to account for the grain size difference, it is seen that nickel increases oxygen grain-boundary transport in alumina by a factor of \( \sim 2 \) (i.e. 3/1.4) in the temperature range studied. This result is not entirely unexpected based on defect chemistry arguments, whereby the incorporation of divalent \( Ni^{2+} \) ions on \( Al^{3+} \) sites could result in the creation of oxygen vacancies, which would enhance oxygen diffusivity. What is perhaps more intriguing is that the value of the corresponding ratio in the Y-doped sample \( (k_2(Y)/k_1(Y)) \) is close to unity at all the temperatures studied. In this case, the average grain sizes of the two layers were within experimental scatter (see Table 1). The implication, therefore, is that, in the presence of \( Y \), the effect of \( Ni \) on enhancing oxygen transport is negated, and the net result is that of Y-doping alone. The reason for this behavior is not understood, but analogous results have been obtained in previous work. Specifically, Drahus et al. [47] observed that, although singly doping with 1000 ppm \( Fe \) reduced the densification rate of alumina, co-doping with \( Y \) and \( Fe \) (1000 ppm each) produced results which were identical to those of Y-doping alone. It was speculated that the preferential segregation of the larger \( Y^{3+} \) ions to the alumina grain boundaries displaced the \( Fe^{3+} \) ions from the near-boundary region and, hence, the influence of the Y-doping predominated. The result that Y-doping can mitigate the influence of other impurities that may be detrimental to scale growth kinetics reveals an additional benefit of RE doping. It also underscores the complexity of the process, and how it can be difficult to isolate the effect of a particular additive when multiple foreign ions are present.

As indicated above, the values of the activation enthalpy for oxidation were within experimental scatter for the undoped alumina wedge layer and the undoped alumina/\( Ni \) substrate. These values were also consistent with those obtained from the previous study on monolithic samples [41]. This self-consistency was also obtained for the values of activation enthalpy for the Y-doped materials (oxide, substrate and monolithic). The presence of the nickel particles, therefore, does not appear to have a strong influence on the magnitude of the activation enthalpy, regardless of whether the alumina contains yttrium. From Eq. (2), note that the rate constant is given in terms of the product of the diffusion coefficient and \( C/C_{Ni} \); it follows therefore, that the activation enthalpy for oxidation is the sum of the activation enthalpies for oxygen grain-boundary diffusion and oxygen surface adsorption. Based on Arrhenius graphs of the data given in Table 2, the values of the activation enthalpies for oxidation and oxygen grain-boundary diffusion differ by only \( \sim 80 \) kJ mol\(^{-1}\).

If we consider the effect of adding yttrium, it can be seen that this resulted in an increase in \( E \) from 407 ± 20 to 486 ± 34 kJ mol\(^{-1}\) in the wedge alumina layer, and from 381 ± 30 to 489 ± 37 kJ mol\(^{-1}\) in alumina/\( Ni \) substrate (an increase of \( \sim 19\% \) and \( 28\% \), respectively). This result contrasts with the findings of Bedu-Amissah et al. [48], who found that although Y-doping decreased the diffusivity for cation (Cr) transport in alumina (by a factor of \( \sim 32 \) at 1300 °C), the activation energy was essentially unchanged. The reason for this difference in behavior is not well understood, especially given the possibility that an oversized dopant could locally distort the grain-boundary region and thereby increase the activation energy. It is also of interest to compare these activation energies with those obtained from tensile creep experiments on similarly prepared samples of undoped and Y-doped alumina [12]. The activation energies obtained from the creep experiments were \( \sim 480 \) kJ mol\(^{-1}\) for undoped alumina and 685 kJ mol\(^{-1}\) for Y-doped alumina. These values, especially for Y-doped alumina, are so much higher than those obtained for oxidation that it leads us to conclude that the dominant mechanisms of creep and oxidation are fundamentally different. Recent first-principles calculations [49] as well as experiments on diffusion vs. grain-boundary sliding rates in bicrystals of undoped and Y-doped alumina [50] suggest that grain-boundary sliding contributes significantly to the creep strain and that the sliding process is more sensitive to Y-doping.

Finally, as noted above, studies of oxygen diffusion in alumina were reviewed by Heuer [40], and it was reported that the published activation energies for oxygen grain-boundary diffusion in alumina range from 310 to 825 kJ mol\(^{-1}\). The broad range in values renders detailed comparison problematic, but one can state that the activation enthalpy values obtained here are consistent with those obtained from experiments on thermally grown oxide on alloys in the temperature range 1000–1200 °C [51,52].

Appendix A

The oxidation kinetics in the bilayer alumina sample can be described by a reaction–diffusion model which reflects oxygen transport and the chemical reaction between nickel and oxygen to form spinel. The bilayer geometry is shown in the schematic in Fig. 5, where the depth of the alumina layer, \( x \), is fixed. For this geometry, the oxygen concentration \( C \) and nickel concentration \( C_{Ni} \) are obtained from the equations

\[
\frac{\partial C}{\partial t} = D_i \frac{\partial^2 C}{\partial z^2} \quad \text{for} \quad 0 < z \leq x
\]

\[
\frac{\partial C}{\partial t} = D_i \frac{\partial^2 C}{\partial z^2} - r(C, C_{Ni}, T) \quad \text{for} \quad z > x
\]

\[
\frac{\partial C_{Ni}}{\partial t} = -r(C, C_{Ni}, T) \quad \text{for} \quad z > x
\]
subject to the initial and boundary conditions

\[
\begin{align*}
C_{\text{Ni}}(t = 0, z \geq x) &= C_{0\text{Ni}}; \\
C(t = 0, z > 0) &= C_0; \\
\frac{D_1}{\partial z^2} |_{z = \infty} &= 0; \\
D_1 \frac{\partial C}{\partial z} |_{z = x_1} &= D_2 \frac{\partial C}{\partial z} |_{z = x_2};
\end{align*}
\]  

(A.2)

where \( C_s \) is oxygen surface concentration (i.e. the oxygen solubility in alumina), \( C_{0\text{Ni}} \) is the initial concentration of Ni in alumina/Ni substrate, and \( D_1 \) and \( D_2 \) are the apparent diffusivities in the alumina top layer and the underlying layer, respectively.

In this description, the reaction kinetics is embodied in the reaction rate \( r(C, C_{\text{Ni}}, T) \) which is assumed to be sufficiently large so that there is only a thin reaction region. In practice, any fast chemical reaction between Ni and O\(_2\) can be employed in the numerical integration of Eq. (A.1). The convenient choice made here is that of second-order reaction kinetics with the corresponding rate \( r = k_r C C_{\text{Ni}} \) [53], where \( k_r \) is the reaction rate constant. For \( k_r \) large, essentially no O\(_2\) will coexist with metallic Ni.

For the purposes of the analysis, it is convenient to recast these equations in dimensionless form. By defining the dimensionless parameters \( \tau = t D_1 / x^2 \), \( z^* = z / x \), \( C^* = C / C_s \), \( x^* = z / x \) and \( \Phi^2 \equiv k_r x^2 C_{0\text{Ni}} / D_1 \), the reaction–diffusion equations become

\[
\begin{align*}
\frac{\partial C^*}{\partial \tau} &= \frac{\partial^2 C^*}{\partial z^*^2} \quad \text{for} \quad 0 < z^* \leq 1 \\
\frac{\partial C^*}{\partial \tau} &= \frac{D_1}{D_2} \frac{\partial^2 C^*}{\partial z^*^2} - \Phi^2 C^* C_{\text{Ni}}^* \quad \text{for} \quad z^* > 1 \\
\frac{\partial C_{\text{Ni}}^*}{\partial \tau} &= -\Phi^2 C^* C_{\text{Ni}}^* \left( \frac{z^*}{x^*} \right) \quad \text{for} \quad z^* > 1
\end{align*}
\]  

(A.3)

The required input parameters for this model include of \( D_2 / D_1 \), \( C_0 / C_{0\text{Ni}} \) and \( \Phi^2 \). In particular, \( \Phi^2 = 500 \) is set to ensure that the reaction zone between oxygen and Ni particles is very thin. Solving these equations numerically using a higher-order finite-difference approximation (i.e. the numerical method of lines) [54], \( C^* \) and \( C_{\text{Ni}}^* \) were calculated for different reduced times \( \tau \), as shown in Fig. A.1. The depth of alumina/spinel layer was calculated via \( y^* = z^* \left(\frac{y}{z} \right)_{y = 1 \times 10^{-3}} - 1 \) where, for practical purposes, the oxygen concentration was taken to be zero when \( C^* < 1 \times 10^{-3} \).

We now return to the data set discussed in Section 3.2 corresponding to a heat treatment of 60 h at 1350 °C (undoped sample) with the aim of using Eq. (A.3) to describe both the transient and quasi-steady-state regimes. In order to compare the experimental data with that obtained using Eq. (A.3), \( xy \) and \( y^2 \) were scaled with \( t D_1 \), where \( t = 60 \) h, and \( D_1 \) was acquired through the best fit to experimental data using Eq. (5). Thus, \( xy / t D_1 \) and \( y^2 / t D_1 \) become the dimensionless parameters \( y^2 / t \) and \( y^2 / t \), respectively. The numerical modeling began with \( D_2 / D_1 = 2.5 \) and \( C_0 / C_{0\text{Ni}} = 0.31 \) in Eq. (A.3), as these parameter values correspond to the best fits to the database using the steady-state and transient equations (Eqs. (2) and (5), respectively). By constructing a \( \chi^2 \) statistic which compared the numerical results with the experimental data in the transient range and then varying the parameters so as to minimize \( \chi^2 \), it was found that \( D_2 / D_1 = 2.5 \) and \( C_0 / C_{0\text{Ni}} = 0.35 \) represent the best fitting parameters. The results are displayed in Fig. A.2, and it can be seen that the numerical data form the characteristic 'C'-shaped curve and that there is good agreement with the experimental data in the transient regime.

The discrepancy between the numerical and the experimental results in the pseudo-steady-state regime may be caused by Ni diffusion into the wedge along the grain boundaries. (It should be noted that the reaction–diffusion model does not incorporate Ni diffusion.) Indeed, in previous oxidation experiments using a monolithic geometry [41], it was noted that a preliminary AEM analysis on alu-

![Fig. A1. Calculated oxygen and Ni concentration profiles in bilayer alumina samples at different times \( \tau (t_1 < t_4) \) using to Eq. (A.3).](image)

![Fig. A2. Comparison of experimental data and numerical results plotted in terms of the dimensionless parameter \( y^2 / t \) (related to the square of the depth of alumina/spinel layer, \( y^2 \)) vs. the dimensionless parameter \( y^2 / t \) (related to the product of the depth of alumina layer and the depth of alumina/spinel layer, \( xy \)) for the wedge sample oxidized at 1350 °C for 60 h.](image)
mina/Ni composites showed Ni segregation to grain boundaries, and that the volume of spinel formed on the free surfaces increased with time. To quantify the amount of outward Ni diffusion, the volume of spinel on the surface of the wedge was monitored from 6 h to 30 h at 1300 °C, using a Dimension 3000 Scanning Probe Microscope (Veeco Instruments Inc., Plainview, NY). The results indicated that the Ni that diffused outward to the surface was 22% of that in the oxidized zone after 24 h at 1300 °C, given a stoichiometric spinel composition. Thus, Ni diffusion may alter the analysis somewhat in the steady-state regime, as a decrease in Ni in the substrate would lead to a greater penetration depth, y, than that predicted by the simplified reaction–diffusion model. The role of Ni diffusion in the wedge-geometry and in the corresponding reaction–diffusion models of oxidation is the subject of ongoing investigations.

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